Chapter – 7

Thermodynamics

I. Choose the correct answer from the following:

Question 1.
The amount of heat exchanged with the surrounding at constant temperature and pressure is called ………
(a) ΔE
(b) ΔH
(c) ΔS
(d) ΔG

Answer:
(b) ΔH

Question 2.
All the naturally occurring processes proceed spontaneously in a direction which leads to
(a) decrease in entropy
(b) increase in enthalpy
(c) increase in free energy
(d) decrease in free energy

Answer:
(d) decrease in free energy

Question 3.
In an adiabatic process, which of the following is true?
(a) $q = w$
(b) $q = 0$
(c) $\Delta E = q$
(d) $P\Delta V = 0$

Answer:
(a) $q = 0$

Question 4.
In a reversible process, the change in entropy of the universe is ‘
(a) >0
(b) > 0
(c) < 0
(d) $= 0$

Answer:
(d) $= 0$

Question 5.
In an adiabatic expansion of an ideal gas
(a) $w = -\Delta u$
(b) $w = \Delta u + \Delta H$
(c) $\Delta u = 0$
(d) $w = 0$

Answer:
(a) $w = -\Delta u$

Question 6.
The intensive property among the quantities below is
(a) mass
(b) volume
(c) enthalpy
(d) mass/volume

Answer:
(d) mass/volume

Question 7.
An ideal gas expands from the volume of 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300K against a constant pressure at 1×10^5 Nm^{-2}. The work done is ………..
(a) – 900 J
(b) 900 kJ
(c) 270 kJ
(d) – 900 kJ

Answer:
(a) – 900 J

Hint:
$w = – P\Delta V$
$w = – (1 \times 105\ Nm^{-2})\ (1 \times 10^{-2}\ m^3 – 1 \times 10^{-3}\ m^3)$
$w = – 10^5\ (10^{-2} – 10^{-3})Nm$
$w = – 10^5\ (10 – 1)\ 10^{3-})\ J$
$w = – 10^5(9 \times 10^{-3})\ J$
$w = – 9 \times 10^2\ J$
$w = – 900\ J$

Question 8.
Heat of combustion is always
(a) positive
(b) negative
(c) zero
(d) either positive or negative

Answer:
(b) negative

Question 9.
The heat of formation of CO and CO_2 are -26.4 kcal and -94 kcal, respectively. Heat of combustion of carbon monoxide will be
(a) +26.4 kcal
(b) -67.6 kcal
(c) -120.6 kcal
(d) +52.8 kcal

Answer:
(b) -67.6 kcal
Hint:
$CO_{(g)} + O_{2(g)} \rightarrow CO_{2(g)}$
$\Delta H_C^0\ (CO) = [\Delta H_f(CO_2) – \Delta H_f(CO) + \Delta H_f(O_2)]$
$\Delta H_C^0\ (CO) = -94\ KCal – [- 26.4\ KCal + 0]$
$\Delta H_C^0\ (CO) = -94\ KCal + 26.4\ KCal$
$\Delta H_C^0\ (CO) = -67.4\ KCal$

Question 10.
C(diamond) → C(graphite), ΔH = -ve, this indicates that ………..
(a) graphite is more stable than diamond
(b) graphite has more energy than diamond
(c) both are equally stable
(d) stability cannot be predicted

Answer:
(a) graphite is more stable than diamond

Question 11.
The enthalpies of formation of Al_2O_3 and Cr_2O_3 are -1596 kJ and -1134 kJ, respectively. ΔH for reaction $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$ is ……….
(a) -1365 kJ
(b) 2730 kJ
(c) -2730 kJ
(d) -462 kJ

Answer:
(d) -462 kJ

Solution:
$2A1 + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$
$\Delta H_r^0 = [2\ \Delta H_f\ (Cr) + \Delta H_f\ (Al_2O_3)] - [2\ \Delta H_f\ (Al) + \Delta H_f\ (Cr_2O_2)]$
$\Delta H_r^0 = [0 + (-\ 1596\ kJ)] - [0 + (-\ 1134)]$
$\Delta H_r^0 = -\ 1596\ kJ + 1134\ kJ$
$\Delta H_r^0 = -\ 462\ kJ$

Question 12.
Which of the following is not a thermodynamic function?
(a) internal energy
(b) enthalpy
(c) entropy
(d) frictional energy

Answer:
(d) frictional energy

Question 13.
If one mole of ammonia and one mole of hydrogen chloride are mixed in a closed container to form ammonium chloride gas, then …………

(a) $\Delta H > \Delta U$
(b) $\Delta H - \Delta U = 0$
(c) $\Delta H + \Delta U = 0$
(d) $\Delta H < \Delta U$

Answer:
(d) $\Delta H < \Delta U$

Question 14.
Change in internal energy, when 4 kJ of work is done on the system and 1 kJ of heat is given out by the system is ………….

(a) +1 kJ
(b) -5 kJ
(c) +3 kJ
(d) -3 kJ

Answer:
(c) +3 kJ
Hint:
$\Delta U = q + w$
$\Delta U = -1\text{ kJ} + 4\text{ kJ}$
$\Delta U = +3\text{ kJ}$

Question 15.
The work done by the liberated gas when 55.85 g of iron (molar mass 55.85 g mol^{-1}) reacts with hydrochloric acid in an open beaker at 25°C …………

(a) -2.48 kJ
(b) -2.22 kJ
(c) +2.22 kJ
(d) + 2.48 kJ

Answer:
(a)-2.48 kJ
Hint:
$Fe + 2HCl \rightarrow FeCl_2 + H_2$

1 mole of Iron liberates 1 mole of hydrogen gas
55.85 g Iron = 1 mole Iron
∴ n = 1
T = 25°C = 298 K

$$w = -P\left(\frac{nRT}{P}\right)$$

w = -nRT
w = -1 x 8314 x 298 J
w = 2477.57 J
w = -2.48 k J

Question 16.
The value of AH for cooling 2 moles of an ideal monoatomic gas from 125°C to 25°C at constant pressure will be [given $C_P = 5/2\ R$] ………….
(a) -250 R
(b) -500 R
(c) 500 R
(d) +250 R

Answer:
(b) -500 R
Hint:
$T_i = 125°C = 398K$
$T_f = 25°C = 298\ K$
$\Delta H = nC_p\ (T_f - T_i)$
$\Delta H = 2 \times 5/2\ R\ (298 - 398)$
$\Delta H = -500\ R$

Question 17.
Given that $C_{(g)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H° = a$ kJ; $2\ CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$ $\Delta H° = -b$ kJ; Calculate the $\Delta H°$ for the reaction $C_{(g)} + H_2O_{2(g)} \rightarrow CO_{(g)}$
(a) $\frac{b+2a}{2}$
(b) 2a – b
(c) $\frac{2a-b}{2}$
(d) $\frac{b-2a}{2}$

Answer:

(d) $\frac{b-2a}{2}$

Hint:

$C + O_2 \rightarrow CO_2$ $\Delta H° = -a$ kJ ……..(1)
$2CO + O_2 \rightarrow 2CO_2$ $\Delta H° = -b$ kJ …….(2)
$C + \frac{1}{2}O_2 \rightarrow CO$ $\Delta H° = ?$
(1) x (2)
$2C + 2O_2 \rightarrow 2CO_2$ $\Delta H° = -2a$ KJ …….(3)
Reverse of equation (2) will be
$2CO_2 \rightarrow 2CO + O_2$ $\Delta H° = +b$ KJ …….(4)
(3) + (4)
$2C + O_2 \rightarrow 2CO$ $\Delta H° = b - 2a$ KJ …….(5)
(5) ÷ 2
$C + O_2 \rightarrow CO$ $\Delta H° = \frac{b-2a}{2}$ KJ

Question 18.

When 15.68 litres of a gas mixture of methane and propane are fully combusted at 0°C and 1 atmosphere, 32 litres of oxygen at the same temperature and pressure are consumed. The amount of heat released from this combustion in kJ is (ΔH_C (CH_4) = – 890 kJ mol^{-1} and ΔH_C (C_3H_8) = -2220 kJ mol^{-1})
(a) -889 kJ
(b) -1390 kJ
(c) -3180 kJ
(d) -653.66 kJ

Answer:

(d) -653.66 kJ
Hint:
Given,
ΔH_C (CH_4) = -890 kJ mol^{-1}
ΔH_C (C_3H_8) = -2220 kJ mol^{-1}
Let the mixture contain x lit of and lit of propane.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
$x \quad 2x$
$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
$(15.68 - x) \quad 5\,(15.68 - x)$
Volume of oxygen consumed = 2 x + 5 (15.68 – x) = 32 lit
2x + 78.4 – 5 x = 321
78.4 – 3x = 32
3x = 46.41
x = 15.471

Given mixture contains 15.47 liters of methane and 0.2 13 liters of propane.
Hence,

$$\Delta H_C = \left[\frac{\Delta H_C(CH_4)}{22.4 \text{ lit}} \times (x) \text{ lit}\right] + \left[\frac{\Delta H_C(C_2H_4)}{22.4 \text{ lit}} \times (3.67 - x) \text{ lit}\right]$$

$$\Delta H_C = \left[\frac{-890 \text{ kJ mol}^{-1}}{22.4 \text{ lit}} \times 1.23 \text{ lit}\right] + \left[\frac{-1423}{22.4 \text{ lit}} \times (3.67 - 1.23) \text{ lit}\right]$$

$\Delta H_C = [- 614.66 \text{ kJ mol}^{-1}] + [- 20.81 \text{ kJ mol}^{-1}]$
$\Delta H_C = 635.47 \text{ kJ mol}^{-1}$.

Question 19.
The bond dissociation energy of methane and ethane are 360 kJ mol^{-1} and 620 Id mol^{-1} respectively. Then, the bond dissociation energy of C-C bond is …………
(a) 170 kJ mol^{-1}
(b) 50 kJ mol^{-1}
(c) 80 kJ mol^{-1}
(d) 220 kJ mol^{-1}

Answer:
(c) 80 kJ mol^{-1}
Hint:
$4E_{C-H} = 360$ kJ mol^{-1}
$E_{C-H} = 90$ kJ mol^{-1}
$E_{C-C} + 6E_{C-H} = 620$ KJ mol^{-1}
$E_{C-C} + 6 \times 90 = 620$ kJ mol^{-1}
$E_{C-C} + 540 = 620$ kJ mol^{-1}
$E_{C-C} = 80$ kJ mol^{-1}

Question 20.
The correct thermodynamic conditions for the spontaneous reaction at all temperature is (NEET phase – I)
(a) $\Delta H<0$ and $\Delta S>0$
(b) $\Delta H<0$ and $\Delta S<0$
(c) $\Delta S>0$ and $\Delta S = 0$
(d) $\Delta H<0$ and $\Delta S>0$

Answer:
(a) $\Delta H<0$ and $\Delta S>0$

Question 21.
The temperature of the system decreases in an ………..
(a) isothermal expansion
(b) isothermal compression
(c) adiabatic expansion
(d) adiabatic compression

Answer:
(c) adiabatic expansion

Question 22.
In an isothermal reversible compression of an ideal gas the sign of q, AS and w are respectively
(a) +, -, –
(b) -, +, –
(c) +, -, +
(d) -, -, +

Answer:
(d) -, -, +
Hint:
During compression, the energy of the system increases, in isothermal condition, to maintain the temperature constant, heat is liberated from the system. Hence q is negative. During compression, entropy decreases. During compression work is done on the system, hence w is positive.

Question 23.
The molar heat of vaporization of a liquid is 4.8 kJ mol^{-1}. If the entropy change is 16 J mol^{-1} K^{-1}. the boiling point of the liquid is ………..
(a) 323 K
(b) 27°C
(c) 164 K
(d) 0.3 K

Answer:
(b) 27°C
Hint:

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$T_b = \frac{\Delta H_V}{\Delta S_V} = \frac{4800 \text{ J mol}^{-1}}{16 \text{ J mol}^{-1}\text{K}^{-1}} = 300 \text{ K} = 27°\text{C}$$

Question 24.
ΔS is expected to be maximum for the reaction
(a) $Ca_{(S)} + O_{2(g)} \rightarrow CaO(S)$
(b) $C_{(S)} + O_{2(g)} \rightarrow CO2(g)$
(c) $N_{2(g)} + O_{2(g)} \rightarrow 2NO(g)$
(d) $CaCO_{3(S)} \rightarrow CaO_{(S)} + CO_{2(g)}$

Answer:
(d) $CaCO_{3(S)} \rightarrow CaO_{(S)} + CO_{2(g)}$
Hint:
In $CaCO_{3(S)} \rightarrow CaO_{(S)} + CO_{2(g)}$ entropy change is positive in (a) and (b) entropy change is negative; in (c) entropy change is zero.

Question 25.
The values of H and S for a reaction are respectively 30 kJ mol^{-1} and loo kJ mol^{-1}. Then the temperature above which the reaction will become spontaneous is …………
(a) 300 K
(b) 30 K
(c) 100 K
(d) 20°C

Answer:
(a) 300 K
Hint:
$\Delta G = \Delta H - T\Delta S$
At 300 K.
$\Delta G = 30000 \text{ J mol}^{-1} - 300 \text{ K} \times 100 \text{ JK mol}^{-1}$
$\Delta G = 0$
above 300 K;
ΔG will be negative and reaction becomes spontaneous.

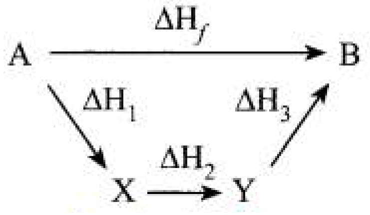
II. Answer these questions briefly.

Question 26.
State the first law of thermodynamics.

Answer:
The first law of thermodynamics, known as the law of conservation of energy, states that the total energy of an isolated system remains constant though it may change from one form to another.
The mathematical statement of the First Law as:
$\Delta U = q + w$
where q – the amount of heat supplied to the system; w – work done on the system.

Question 27.
Define Hess's law of constant heat summation.

Answer:
Hess's law:
The enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single or multiple steps.



$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3$

Question 28.
Explain intensive properties with two examples.

Answer:
The property that is independent of the mass or the size of the system is called an intensive property. Refractive index, Surface tension, density, temperature, Boiling point, Freezing point, molar volume.

Question 29.
Define the following terms:
(a) isothermal process
(b) adiabatic process
(c) isobaric process
(d) isochoric process

Answer:
a. An isothermal process is defined as one in which the temperature of the system remains constant, during the change from its initial to final state. The system exchanges heat with its surroundings and the temperature of the system remains constant. For an isothermal process $dT = 0$.

b. An adiabatic process is defined as one in which there is no exchange of heat (q) between the system and surrounding during the process. Those processes in which no heat can flow into or out of the system are called adiabatic processes.

c. An isobaric process is defined as one in which the pressure of the system remains constant during its change from the initial to final state.
For an isobaric process $dP = 0$.

d. An isochoric process is defined as the one in which the volume of system remains constant during its change from initial to final state. Combustion of fuel in a bomb calorimeter is an example of an isochoric process.
For an isochoric process, $dV= 0$.

Question 30.
What is the usual definition of entropy? What ¡s the unit of entropy?

Answer:

1. Entropy is a thermodynamic state function that is a measure of the randomness or disorderliness of the system.
2. For a reversible change taking place at a constant temperature (T). the change in entropy
3. of the system is equal to heat energy absorbed or evolved (q) by the system divided by the constant temperature (T).
   $$\Delta S_{sys} = \frac{q_{rev}}{T}$$
4. SI unit of entropy is J K^{-1}

Question 31.
Predict the feasibility of a reaction when

1. both ΔH and ΔS positive
2. both ΔH and ΔS negative
3. AH decreases but ΔS increases

Answer:

1. ΔH_r = + ve, ΔS = + ve; non-spontaneous at low temperature spontaneous at high temperature
2. ΔH_r = – ve, ΔS = – ve; spontaneous at low temperature non-spontaneous at high temperature
3. ΔH decreases but ΔS increases = Spontaneous at all temperatures.

Question 32.
Define Gibb's free energy.

Answer:
G is expressed as G = H – TS, free energy change of a process is given by the relation ΔG = ΔH – TΔS.

Question 33.
Define enthalpy of combustion.

Answer:
Enthalpy of combustion of a substance is defined as “the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen”. it is denoted as AH.

Question 34.
Define molar heat capacity. Give its unit.

Answer:
Molar heat capacity is defined as “the amount of heat absorbed by one mole of a substance in raising the temperature by I Kelvin”. It is denoted as C_m
Unit of Molar heat capacity: SI unit of C_m is JK^{-1} mol^{-1}.

Question 35.
Define the calorific value of food. What is the unit of calorific value?

Answer:

- The calorific value of food is defined as the amount of heat produced in calories (or Joules) when one gram of food is completely burnt.
- Unit of calorific value (a) Cal g^{-1} (b) J Kg^{-1}

Question 36.
Define enthalpy of neutralization.

Answer:
The heat of neutralization is defined as “The change in enthalpy when one gram equivalent of an acid is completely neutralized by one gram equivalent of a base or vice versa in dilute solution”.
$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O$
$\Delta H = -57.32$ kJ

Question 37.
What is lattice energy?

Answer:
Lattice energy is defined as the amount of energy required to completely separate one mole of a solid ionic compound into a gaseous constituent.

Question 38.
What are state and path functions? Give two examples.

Answer:

State function:
A state function is a thermodynamic property of a system, which has a specific value for a given state and does not depend on the path (or manner) by which the particular state is reached.

Example:
Pressure (P), Volume (V), Temperature(T), Internal energy (U), Enthalpy (H), free energy (G) etc.

Path functions:
A path function is a thermodynamic property of the system whose value depends on the path by which the system changes from its initial to final states.
Examples: Work (w), Heat (q).

Question 39.
Give Kelvin a statement of the second law of thermodynamics.

Answer:
It is impossible to construct a machine that absorbs heat from a hot source and converts it completely into work by a cyclic process without transferring a part of heat to a cold sink.

Question 40.
The equilibrium constant of a reaction is 10, what will be the sign of ΔG? Will this reaction be spontaneous?

Answer:
$\Delta G^\circ = -2.303\ RT \log K_{eq}$
$K_{eq} = 10$
$\therefore \Delta G^\circ =$ -ve value.
So the reaction will be spontaneous.

Question 41.
Enthalpy of neutralization is always a constant when a strong acid is neutralized by a strong base: account for the statement.

Answer:
It is because in dilution solution all strong acids and strong bases are completely ionized. The neutralization of strong acid and strong bases are completely ionized. The neutralization of a strong acid and strong base simply involves the combination of H^+ ions (from acid) and OH^- ions (from base) to form unionized water molecules with the evolution of 57.1 kJ heat.
$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O(l)$,
$\Delta_2H° = -57.1$ kJ
Since the same reaction takes place during neutralization of all strong acids and strong bases, the value of enthalpy of neutralization is constant.

Question 42.
State the third law of thermodynamics.

Answer:
It states that the entropy of pure crystalline substance at absolute zero is zero. (or). It can be stated as “it is impossible to lower the temperature of an object to absolute zero in a finite number of steps”. Mathematically $\lim_{T \rightarrow 0} S = 1$

Question 43.
Write down the Born-Haber cycle for the formation of $CaCl_2$

Answer:
Born – Haber cycle for the formation of $CaCl_2$
$Ca_{(S)} + Cl_{2(l)} \rightarrow CaC_{2(S)}$ $\Delta H_f°$
Sublimation : $Ca_{(S)} \rightarrow Ca_{(S)}$ $\Delta H_1°$
Ionization : $Ca_{(g)} \rightarrow Ca^{2+}_{(g)} + 2e^- = \Delta H_2°$
Vapourisation : $Cl_{2(l)} \rightarrow Cl_{2(g)} = \Delta H_3°$
Dissociation : $Cl_{2(g)} \rightarrow 2Cl_{(g)} = \Delta H_4°$
Electron affinity : $2Cl_{2(g)} + 2e^- \rightarrow 2Cl^{-2(g)}_{(g)} = \Delta H_5°$
Lattice enthalpy : $Ca^{2+}_{(g)} + 2Cl^-_{(g)} \rightarrow CaCl_{2(S)} = \Delta H_6°$
$\Delta H_f° = \Delta H_1° + \Delta H_2° + \Delta H_3° + \Delta H_4° + \Delta H_5° + \Delta H_6°$

Question 44.
Identify the state and path functions out of the following
(a) Enthalpy
(b) Entropy
(c) Heat
(d) Temperature
(e) Work
(f) Free energy.

Answer:
State function: Enthalpy, entropy, temperature, and free energy.
Path function: Heat and work.

Question 45.
State the various statements of the second law of thermodynamics.

Answer:
Entropy statement:
The second law of thermodynamics can be expressed in terms of entropy, i.e "the entropy of an isolated system increases during a spontaneous process".

Kelvin-Planck statement:
It is impossible to construct a machine that absorbs heat from a hot source and converts it completely into work by a cyclic process without transferring a part of heat to a cold sink.

Clausius statement:
It is impossible to transfer heat from a cold reservoir to a hot reservoir without doing some work.

Question 46.
What are spontaneous reactions? What are the conditions for the spontaneity of a process?

Answer:

1. A reaction that does occur under the given set of conditions is called a spontaneous reaction.

2. The expansion of a gas into an evacuated bulb is a spontaneous process, the reverse process that is gathering of all molecules into one bulb is not spontaneous. This example shows that processes that occur spontaneously in one direction cannot take place in opposite direction spontaneously.
3. Increase in randomness favours a spontaneous change.
4. If enthalpy change of a process is negative, then the process is exothermic and occurs spontaneously. Therefore ΔH should be negative.
5. if entropy change of a process is positive, then the process occurs spontaneously, therefore ΔS should be positive.
6. If free energy of a process is negative, then the process occurs spontaneously, therefore ΔG should be negative.
7. For a spontaneous. irreversible process. $\Delta H < 0$, $\Delta S > 0$, $\Delta G < 0$. i.e., ΔH = -ve, ΔS = +ve and ΔG = -ve.

Question 47.
List the characteristics of internal energy.

Answer:
The internal energy of a system is an extensive property. It depends on the amount of the substances present in the system. If the amount is doubled, the internal energy is also doubled.

The internal energy of a system is a state function. It depends only upon the state variables (T, P, V, n) of the system. The change in internal energy does not depend on the path by which the final state is reached.

The change in internal energy of a system is expressed as $\Delta U = U_f - U_i$.
In a cyclic process, there is no internal energy change. $\Delta U_{(cyclic)} = 0$
If the internal energy of the system in the final state (U_f) is less than the internal energy of the system in its initial state (U_i), then ΔU would be negative.

$\Delta U = U_f - U_i$ = -ve($U_f < U_i$)
If the internal energy of the system in the final state (U_f) is greater than the internal energy of the system in its initial state (U_i), then ΔU would be positive.
$\Delta U = U_f - U_i$ = + ve($U_f > U_i$).

Question 48.
Explain how heat absorbed at constant volume is measured using a bomb calorimeter with a neat diagram.

Answer:

1. For chemical reactions, heal absorbed at constant volume, is measured in a bomb calorimeter.

2. Description of the apparatus and procedure:

The inner vessel and its cover are made of strong steel. The cover is fitted tightly to the vessel by means of metal lid and screws. A weighed amount of the substance is taken in a platinum cup connected with electrical wires for striking an arc instantly to kindle combustion. The bomb is then tightly closed and pressurizcd with excess

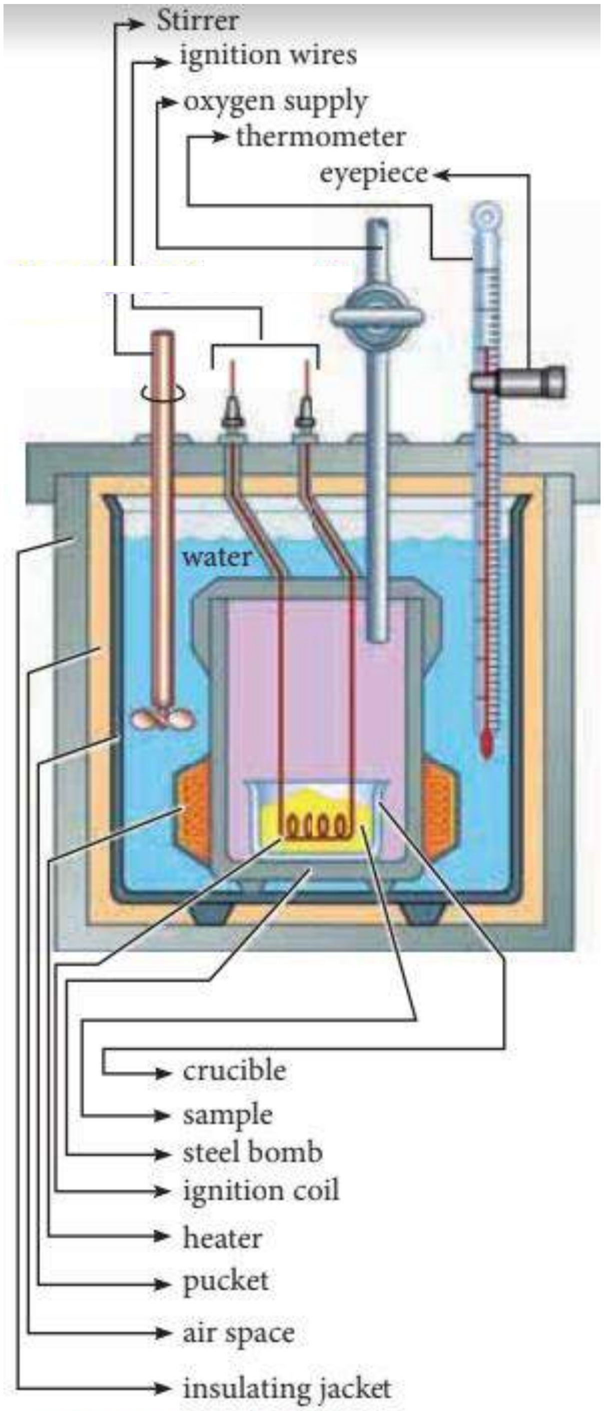
$$P_{\text{ext}} = \frac{\text{Force (F)}}{\text{Area (A)}} \text{ ....(2)}$$

oxygen. The bomb is lowered in water, which is placed inside the calorimeter.

A stirrer is placed in the bomb to stir the water uniformly. The reaction is started by striking the substance through electrical heating.

3. During burning, the exothermic heat generated inside the bomb raises the temperature of the surrounding water bath. Temperature change can be measured accurately using Beckmann thermometer.

Since the bomb calorimeter is sealed, its volume does not change, so the heat measurements, in this case, corresponds to the heat of reaction at constant volume.



Bomb calorimeter

4. In a bomb calorimeter experiment, a weighed sample of benzoic acid (w) is placed in the bomb which is then filled with excess oxygen and sealed. Ignition is brought about electrically. The rise in temperature (AT) is noted. Water equivalent or calorimetry equivalent of the calorimeter is known from the standard value of enthalpy of combustion of benzoic acid.

5. $\Delta H_C(C_6H_5COOH) = -3227$ kJ mol^{-1}

$$\omega_e = \frac{\Delta H_C(C_6H_5COOH)}{\Delta T} \times \frac{W}{M_2}$$

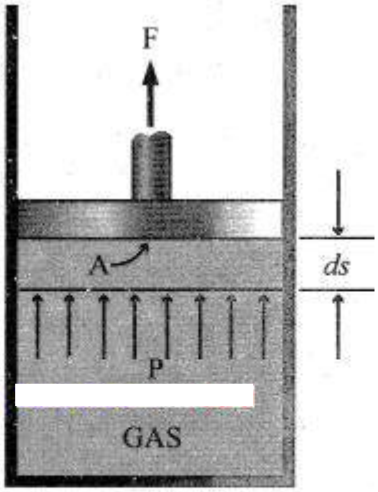
6. By knowing o value, the enthalpy of combustion of any other substance is determined adopting the similar procedure and using the substance in place of’ benzoic acid. By this experiment, the enthalpy of combustion at constant volume (AU_C°) is known,
$\Delta U_C^\circ = \omega_e . \Delta T$

7. Enthalpy of combustion at constant pressure of the substance is calculated from the equation
$\Delta U^\circ_{C(pressure)} = \Delta U^\circ_{C(volume)} + \Delta n_g RT$

Question 49.
Calculate the work involved in the expansion and compression process.

Answer:
1. The essential condition of expansion or compression of a system is, there should be a difference between external pressure P_{ext} and internal pressure (P_{int}).

2. If the volume of the system is increased against the external pressure. the work is done by the system. By convention work done by the system is given a negative sign (-w).



3. If the volume of the system decreased, the work is done on the system. By convention work done on the system is given a positive sign (+w).

4. For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is P_{int}.

5. If external pressure is P_{ext} which is greater than P_{int} piston is moved inward till the pressure inside becomes equal to P_{int} It is achieved in a single step and the final volume be V_f.

6. During this compression, piston moves a distance x) and is the cross-sectional area of the piston is A, then, Change in volume = x A = $\Delta V = V_f - V_i$ ………..(1)

$$P_{ext} = \frac{Force(F)}{Area(A)} \text{ ………(2)}$$

$$F = P_{ext}.A$$

7. if work is done by the system by pushing out the piston against external pressure (P_{ext}) then according to the equation,
$-w = F.x$ ………(3)
$-w = P_{ext} . A . x$ …….(4)
$-w = P_{ext}.\Delta V$ ……….(5)
$-w = P_{ext} . (V_f - V_i.)$ …..(6)
Simply $w = - P\Delta V$ ………..(7)

8. From the above equation, we can predict the sign of work (w).

9. During expansion, work is done by the system, since $V_f > V_i$ the sign obtained for work will be negative.

10. During compression, work is done on the system, since $V_f < V_i$ the sign obtained for work will be positive.

Question 50.
Derive the relation between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.

Answer:

When the system at constant pressure undergoes changes from an initial state with H_1, U_1 and V_1 to a final state with H_2, U_2 and V_2 the change in enthalpy ΔH can be calculated as follows:

$H = U + PV$

In the initial state

$H_1 = U_1 + PV_1$ ………………(1)

In the final state

$H_2 = U_2 + PV_2$ ……………..(2)

change in enthalpy is (2) – (1)

$(H_2 - H_1) = (U_2 - U_1) + P(V_2 - V_1)$

$\Delta H = \Delta U + P\Delta V$ ………………..(3)

As per first law of thermodynamics,

$\Delta U = q + w$

Equation (3) becomes

$\Delta H = q + w + P\Delta V$

$w = -P\Delta V$

$\Delta H = qp - P\Delta V + P\Delta V$

$\Delta H = qp$ …………..(4)

qp – is the heat absorbed at constant pressure and is considered as heat content.

Consider a closed system of gases which are chemically reacting to form gaseous products at constant temperature and pressure with V_i and V_f, as the total volumes of the reactant and product gases respectively, and niand nfas the number of moles of gaseous reactants and products, then,

For reactants (initial state):

$PV_i = n_iRT$ ………..(5)

For products (final state):

$PV_f = n_fRT$ ……………..(6)

(6) – (5)

$P\{V_f - V_i) = (n_f - n_i)RT$

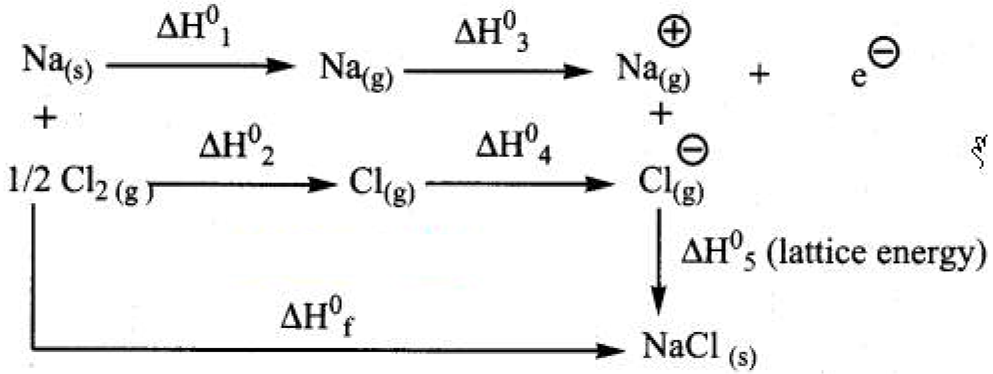
$P\Delta V = \Delta n_{(g)} RT$ ………..(7)

Substituting in (7) in (3)

$\Delta H = \Delta U + \Delta n_{(g)}RT$ …………….(8)

Question 51.
Suggest and explain an indirect method to calculate lattice enthalpy of sodium chloride crystal.

Answer:
The Born – Haber cycle is used to determine the lattice enthalpy of NaCl as follows:



Formation of NaCl can be considered in 5 steps. The sum of the enthalpy changes of these steps is equal to the enthalpy change for the overall reaction from which the lattice enthalpy of NaCl is calculated.

$Na_{(s)}$ + Vi $Cl_{2(g)} \rightarrow NaCl_{(s)}$ $\Delta H_f = -411.3$ kJ mol^{-1}
Sublimation : $Na_{(s)} \rightarrow Na_{(g)}$ $\Delta H_1°$
Dissociation : ½ $Cl_{2(g)} \rightarrow Cl_{(g)}$ $\Delta H_2°$
Ionisation : $Na_{(s)} \rightarrow Na^+_{(g)} + e^-$ $\Delta H_3°$

E1etron affinity : $Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$ $\Delta H_4°$
Lattice enthalpy : $Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$ $\Delta H_5° =?$
$\Delta H = \Delta H_1° + \Delta H_4° + \Delta H_4° + \Delta H_4° + \Delta H_4°$
$\Delta H = \Delta H_f° - (\Delta H_1° + \Delta H_2° + \Delta H_3° + \Delta H_4°)$
$\Delta H_5°$= Lattice enthalpy of NaCl.

By the above method, indirectly lattice enthalpy of NaCl is calculated if the values of $\Delta H_f°$, $\Delta H_1°$, $\Delta H_2°$- $\Delta H_3°$ and $\Delta H_4°$ are given.

Question 52.
List the characteristics of Gibbs free energy.

Answer:
(i) G is defined as (H-TS) where H and S are the enthalpy and entropy of the

system respectively. T = temperature. Since H and S are state functions, G is a state function.

(ii) G is an extensive property while $\Delta G = (G_2 - G_1)$ which is the free energy change between the initial (1) and final (2) states of the system becomes the intensive property when mass remains constant between initial and final states (or) when the system is a closed system.

(iii) G has a single value for the thermodynamic state of the system.

(iv) G and ΔG values correspond to the system only. There are three cases of ΔG in predicting the nature of the process. When, $\Delta G < 0$ (negative), the process is spontaneous and feasible; $\Delta G = 0$. The process is in equilibrium and $\Delta G > 0$ (positive), the process is nonspontaneous and not feasible.

(v) $\Delta G = \Delta H - T\Delta S$. But according to I law of thermodynamics,
$\Delta H = \Delta G + P\Delta V$ and $\Delta U = q + w$
$\therefore \Delta G = q + w + P\Delta V - T\Delta S$
But $\Delta S = T/q$ and $T\Delta S = q$ = heat involved in the process.
$\therefore \Delta G = q + w + P\Delta V - q = w + P\Delta V$
(or) $- \Delta G = - w - P\Delta V$ = network.

The decrease in free energy $- \Delta G$, accompanying a process taking place at constant temperature and pressure is equal to the maximum obtainable work from the system other than work of expansion.
This quantity is called the “network” of the system and it is equal to $(- w - P\Delta V)$.

$\therefore$ Network $= - w - P\Delta V$
$-\Delta G$ represents all others forms of work obtainable from the system such as electrical, chemical or surface work etc other than P-V work.

Question 53.
Calculate the work done when 2 moles of an ideal gas expands reversibly and isothermally from a volume of 500 ml to a volume of 2 L at 25°C and normal pressure.

Answer:
Given
n = 2 moles
V_i = 500 ml = 0.5 lit
V_f = 2 lit
T = 25°C = 298 K

$$w = -2.303 \text{ nRT log} \left(\frac{V}{V_i}\right)$$

$$w = -2.303 \times 2 \times 8.314 \times 298 \times \log \frac{2}{0.5}$$

$$w = -2.303 \times 2 \times 8.314 \times 298 \times \log(4)$$

$$w = -2.303 \times 2 \times 8.314 \times 298 \times 0.6021$$

$$w = -6871 \text{ J}$$

$$w = -6.871 \text{ kJ.}$$

Question 54.
In a constant-volume calorimeter, 3.5 g of gas with molecular weight 28 was burnt ¡n excess oxygen at 298 K. The temperature of the calorimeter was found to increase from 298 K to 298.45 K due to the combustion process. Given that the calorimeter constant is 2.5 kJ K^{-1}. Calculate the enthalpy of combustion of the gas in kJ mol^{-1}.

Answer:
Given
T_i = 298 K
T_f = 298.45 K
k = 2.5 kJ K^{-1}
m = 3.5g
Mm = 28
heat evolved = kΔT
= $k(T_f - T_i)$
= 2.5KJ K^{-1} (298.45 – 298)K = 1.125 kJ

$$\Delta H_c = \frac{1.125}{3.5} \times 28 \text{ kJ mol}^{-1}$$

$$\Delta H_c = 9 \text{ kJmol}^{-1}$$

Question 55.
Calculate the entropy change in the system and surroundings and the total entropy change in the universe during a process in which 245 J of heat flow out of the system at 77°C to the surrounding at 33°C.

Answer:
Given:
$T_{sys} = 77°C = (77 + 273) = 350K$
$T_{sys} = 33°C = (33 + 273) = 306K$
$q = 245$ J

$$\Delta S_{sys} = \frac{q}{T_{sys}} = \frac{-245}{350} = -0.7\ JK^{-1}$$

$$\Delta S_{univ} = \frac{q}{T_{sys}} = \frac{+245}{350} = +0.8\ JK^{-1}$$

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$-245 = —07 3K’
$\Delta S_{univ} = -0.7\ JK^{-1} + 0.8\ JK^{-1}$
$\Delta S_{univ} = 0.1\ JK^{-1}$

Question 56.
1 mole of an ideal gas, maintained at 4.1 atm and at a certain temperature, absorbs heat 3710 J and expands to 2 litres. Calculate the entropy change in expansion process.

Answer:
Given,
n = 1 mole
P = 4.1 atm
V = 2Lit
T = ?
q = 3710 J
$\Delta S = q/T$

$$\Delta S = \frac{q}{\left(\frac{PV}{nR}\right)}$$

$$\Delta S = \frac{nRq}{PV}$$

$$\Delta S = \frac{1 \times 0.082 \text{ lit atm K}^{-1} \times 3710 \text{ J}}{4.1 \text{ atm} \times 2 \text{ lit}}$$

$\Delta S = 37.10 \text{ JK}^{-1}$

Question 57.

30.4 kJ is required to melt one mole of sodium chloride. The entropy change during melting is 28.4 JK^{-1} mol^{-1}. Calculate the melting point of sodium chloride.

Answer:

Given,

$\Delta H_f(\text{NaCl}) = 30.4 \text{ kJ} = 30400 \text{ J mol}^{-1}$

$\Delta S_f (\text{NaCl}) = 28.4 \text{ JK}^{-1} \text{ mol}^{-1}$

$T_f = ?$

$$\Delta S_f = \frac{\Delta H_f}{\Delta T_f}$$

$$T_f = \frac{\Delta H_f}{\Delta S_f}$$

$$T_f = \frac{30400 \text{ J mol}^{-1}}{28.4 \text{ J K}^{-1}\text{mol}^{-1}}$$

$T_f = 1070.4$ K.

Question 58.

Calculate the standard heat of formation of propane, if its heat of combustion is -2220.2 KJ mol^{-1}, the heats of formation of $CO_{2(g)}$ and $H_2O_{(l)}$ are – 393.5 and -285.8 kJ mol^{-1} respectively.

Answer:

Given,

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

$\Delta H_C^0 = -2220.2 \text{ kJ mol}^{-1}$ ....(1)

$C + O_2 \rightarrow CO_2$

$\Delta H_f^0 = -393.5 \text{ kJ mol}^{-1}$ ....(2)

$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

$\Delta H_f^0 = -285.8 \text{ kJ mol}^{-1}$ ....(3)

$3C + 4H_2 \rightarrow C_3H_8$

$\Delta H_C^0 = ?$

$(2) \times 3 \Rightarrow 3C + 3O_2 \rightarrow 3CO_2$

$\Delta H_f^0 = -1180.5 \text{ kJ}$ ....(4)

$(3) \times 4 \Rightarrow 4H_2 + 2O_2 \rightarrow 4H_2O$

$\Delta H_f^0 = -1143.2 \text{ kJ}$ ....(5)

$(4) + (5) - (1)$

$\Rightarrow 3C + 3O_2 + 4H_2 + 2O_2 + 3CO_2 + 4H_2O \rightarrow 3CO_2 + 4H_2O + C_3H_8 + 5O_2$

$\Delta H_f^0 = -1180.5 - 1143.2 - (-2220.2) \text{ kJ}$

$3C + 4H_2 \rightarrow C_3H_8$

$\Delta H_f^0 = -103.5 \text{ kJ mol}^{-1}$

The standard heat of formation of propane is $\Delta H_f^0(C_3H_8) = -103.5 \text{ kJ mol}^{-1}$.

Question 59.

You are given normal boiling points and standard enthalpies of vaporization. Calculate the entropy of vaporization of liquids listed below.

S.No.	Liquid	Boiling points (°C)	ΔH (kJ mol^{-1})
1.	Ethanol	78.4	+ 42.4
2.	Toluene	110.6	+ 35.2

Answer:

For ethanol:

Given:

$T_b = 78.4°C = (78.4 + 273) = 351.4 \text{ K}$

$\Delta H_v(\text{ethanol}) = + 42.4 \text{ kJ mol}^{-1}$

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$\Delta S_V = \frac{+ 42.4 \text{ kJ mol}^{-1}}{351.4 \text{ K}}$$

$$\Delta S_V = \frac{+ 42400 \text{ J mol}^{-1}}{351.4 \text{ K}}$$

$\Delta H_v = + 91.76$ J K^{-1} mol^{-1}

For Toluene:

Given:

$T_b = 110.6°C = (110.6 + 273) = 383.6$ K

ΔS_V (toluene) = + 35.2 KJ mol^{-1}

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$\Delta S_V = \frac{+ 35.2 \text{ kJ mol}^{-1}}{383.6 \text{ K}}$$

$$\Delta S_V = \frac{+ 35200 \text{ J mol}^{-1}}{383.6 \text{ K}}$$

$\Delta S_V = + 91.76$ J KJ mol^{-1}

Question 60.

For the reaction $Ag_2O_{(s)} \rightarrow 2Ag_{(s)} + ½ O_{2(g)}$: $\Delta H = 30.56$ kJ mol^{-1} and $\Delta S = 6.66$ JK^{-1} mol^{-1} (at 1 atm). Calculate the temperature at which AG is equal to zero. Also predict the direction of the reaction (i) at this temperature and (ii) below this temperature.

Answer:

Given,

$\Delta H = 30.56$ kJ mol^{-1}

$\Delta H = 30560$ J mol^{-1}

$\Delta S = 6.66 \times 10^{-3}$ kJ K^{-1} mol^{-1}

T = ? at which $\Delta G = 0$

$\Delta G = \Delta H - T\Delta S$

$0 = \Delta H - T\Delta S$

$T = \Delta H \Delta S$

$$T = \frac{30.56 \text{ kJ mol}^{-1}}{6.66 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}}$$

T = 4589K

(i) At 4589K ; $\Delta G = 0$, the reaction is in equilibrium.

(ii) At temperature below 4598 K, $\Delta H > T \Delta S$
$\Delta G = \Delta H - T\Delta S > 0$, the reaction in the forward direction, is non-spontaneous. In other words the reaction occurs in the backward direction.

Question 61.
What is the equilibrium constant K_{eq} for the following reaction at 400K.
$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$ given that AH° = 77.2 kJ mol^{-1} and $\Delta S° = 122$ JK^{-1} mol^{-1}

Answer:
Given,
T = 400 K ; $\Delta H° = 77.2$ kJ mol^{-1} = 77200 J mol^{-1};
$\Delta S° = 122$ JK^{-1} mol^{-1}
$\Delta G° = -2.303$ RT log K_{eq}

$$\log K_{eq} = \frac{\Delta G^0}{2.303\ RT}$$

$$\log K_{eq} = -\frac{\left(\Delta H^0 - T\Delta S^0\right)}{2.303\ RT}$$

$$\log K_{eq} = -\left(\frac{77200 - 400\ \times 122}{2.303 \times 8.314 \times 400}\right)$$

$$\log K_{eq} = -\left(\frac{28400}{7659}\right)$$

log K_{eq} = -3.7080
K_{eq} = anti log(-3.7080)
$K_{eq} = 1.95 \times 10^{-4}$

Question 62.
Cyan-amide (NH_2CN) ¡s completely burnt in excess oxygen in a bomb calorimeter, ΔU was found to be -742.4 kJ mol^{-1} calculate the enthalpy change of the reaction at 298K.
$NH_2CN_{(s)} + 3/2\ O_{2(g)} \rightarrow N_{2(g)} + CO_{2(g)} + H_2O_{(l)}\ \Delta H = ?$

Answer:
Given

T = 298 K;

$\Delta U = -742.4 \text{ kJ mol}^{-1}$

$\Delta H = ?$

$\Delta H = \Delta U + \Delta n_{(g)}RT$

$\Delta H = \Delta U + (n_p - n_r)RT$

$\Delta H = 742.4 + 2 - 3/2 \times 8.314 \times 10^{-3} \times 298$

$= -742.4 + (0.5 \times 8.314 \times 10^{-3} \times 298)$

$= -742.4 + 1.24$

$= -741.16 \text{ kJ mol}^{-1}$

Question 63.

Calculate the enthalpy of hydrogenation of ethylene from the following data. Bond energies of C H, C – C, C = C and H – H are 414, 347, 618 and 435 kJ mol^{-1}.

Answer:

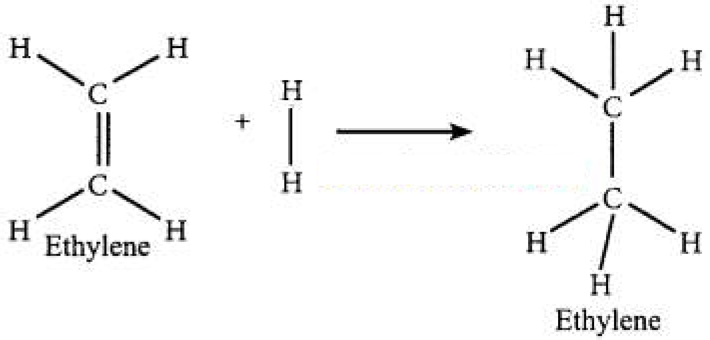
Given,

$E_{C-H} = 414 \text{ kJ mol}^{-1}$

$E_{C-H} = 347 \text{ kJ mol}^{-1}$

$E_{C-H} = 618 \text{ kJ mol}^{-1}$

$E_{H-H} = 435 \text{ kJ mol}^{-1}$



$\Delta H_r = \sum(\text{Bond energy})_r - \sum(\text{Bond energy})_P$

$\Delta H_r = (E_{C=C} + 4E_{C-H} + E_{H-H}) - (E_{C-C} + 6E_{C-H})$

$\Delta H_r = (618 + (4 \text{ x } 414) + 435) - (347 + (6 \text{ x } 414))$

$\Delta H_r = 2709 - 2831$

$\Delta H_r = -122 \text{ KJ mol}^{-1}$

Question 64.

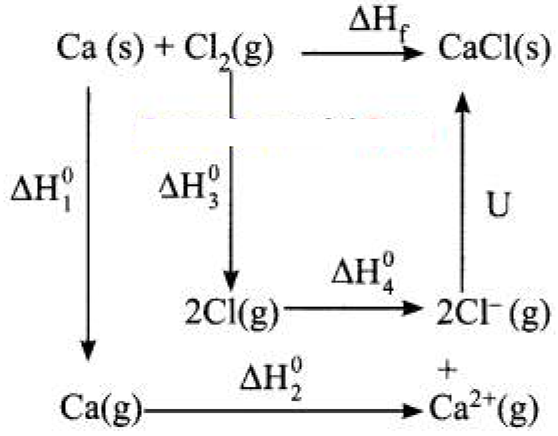
Calculate the lattice enegry of $CaCl_2$ from the given data

$Ca_{(s)} + Cl_{2(g)} \rightarrow CaCl_{2(s)} \;\; \Delta H_f^0 = -795 \text{ KJ mol}^{-1}$

Atomisation : $Ca_{(s)} \rightarrow Ca_{(g)} \;\; \Delta H_1° = + 121 \text{ KJ mol}^{-1}$

Ionization : $Ca_{(g)} \rightarrow Ca^{2+}_{(g)} + 2e^{-}$ $\Delta H_2^\circ = +\ 242.8$ KJ mol^{-1}
Dissociation : $Cl_{2(g)} \rightarrow 2\ Cl_{(g)}$ $\Delta H_3^\circ = +242.8$ KJ mol^{-1}
Electron affinity : $Cl_{(g)} + e^{-} \rightarrow Cl^{-}_{(g)}$ $\Delta H_3^\circ = -355$ KJ mol^{-1}

Answer:



$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + 2\Delta H_4 + u$
$-795 = 121 + 2422 + 242.8 + (2\ x—355) + u$
$-795 = 2785.8 - 710 + u$
$-795 = 2075.8 + u$
$u = -795 - 2075.8$
$u = -2870.8$ KJ mol^{-1}

Question 65.

Calculate the enthalpy change for the reaction $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ from the following data.
$2Fe + 3/2\ O_2 \rightarrow Fe_2O_3$; $\Delta H = -741$ kJ
$C + 1/2\ O_2 \rightarrow CO$; $\Delta H = -137$ KJ
$C + O_2 \rightarrow CO_2$ $\Delta H = -394.5$ KJ

Answer:

Given,
$\Delta H_f\ (Fe_2O_3) = -741$ kJ mol^{-1}
$\Delta H_f(CO) = -137$ kJ mol^{-1}
$\Delta H_f(CO_2) = -394.5$ kJ mol^{-1}
$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ $\Delta Hr = ?$
$\Delta Hr = \sum(\Delta H_f)_{products} - \sum(\Delta H_f)_{reactants}$
$\Delta Hr = [2\ \Delta H_f(Fe) + 3\ \Delta H_f(CO_2)] - [\Delta H_f(Fe_2O_3) + 3\Delta H_f(CO)]$
$\Delta Hr = [-\ 1183.5\ ] - [-1152]$

$\Delta Hr = - 1183.5 + 1152$
$\Delta Hr = -31.5$ KJ mol^{-1}

Question 66.
When 1-pentyne (A) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 13% 1-pentyne(A), 95.2% 2-pentyne(B) and 3.5% of 1,2 pentadiene (C) the equilibrium was maintained at 175°C, calculate AG° for the following equilibria.
$B \rightleftharpoons A \; \Delta G_1° = ?$
$B \rightleftharpoons C \; \Delta G_2° = ?$

Answer:
Given
T = 175°
C = 175 + 273 = 448 K
Concentration of 1-pentyne [A] = 1.3%
Concentration of 2-pentyne [B] = 95.2%
Concentration of 1, 2-pentadiene [C] = 3.5%

At equilibrium
$B \rightleftharpoons A$
95.2% 1.3% ⇒
$B \rightleftharpoons C$
95.2% 3.5% ⇒
$K_2 = 3.5/95.2 = 0.0367$
$\Rightarrow \Delta G°_1 = -2.303 \, RT \log K$
$\Delta G°_1 = - 2.303 \times 8.314 \times 448 \times \log 0.0136$
$\Delta G°_1 = +16010$ J
$\Delta G°_1 = +16$ kJ

$\Rightarrow \Delta G°_2 = - 2.303 \, RT \log K_2$
$\Delta G°_2 = -2.303 \times 8.314 \times 448 \times \log 0.0367$
$\Delta G°_2 = +12312$J
$\Delta G°_2 = +12.312$ kJ

Question 67.
At 33K. N_2H_4 is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

Answer:
T = 33K
$N_2O_4 \rightleftharpoons 2NO_2$
Initial concentration 100%
Concentration dissociated 50%
Concentration remaining at equilibrium 50% – 100%
$K_{eq} = 100/50 = 2$
$\Delta G° = -2.303 \text{ RT} \log K_{eq}$
$\Delta G° = -2.303 \times 8.31 \times 33 \times 1\text{og } 2$
$\Delta G° = -190.18 \text{ J mol}^{-1}$

Question 68.
The standard enthaipies of formation, of SO_2 and SO_3 are -297, kJ. rnol^{-1} and -396 kJ mol^{-1} respectively. Calculate the standard enthalpy of reaction for the reaction:
$SO_2 + 1/2 \ O_2 \rightarrow SO_3$

Answer:
Given
$\Delta H°_f(SO_2) = – 297 \text{ kJ mol}^{-1}$
$\Delta H°_f(SO_3) = – 396 \text{ kJ mol}^{-1}$
$SO_2 + 12O_2 \rightarrow SO_3;$
$\Delta H°_r =?$
$\Delta H°_r = (\Delta H°_f)_{compound} – \Sigma(\Delta H_f)_{elements}$
$\Delta H°_r = \Delta H°_r(SO_3) – \Delta H°_f$
$\Delta H°_r = 396 \text{ kJ mol}^{-1} – (- 297 \text{ kJ mol}^{-1} + 0)$
$\Delta H°_r = – 396 \text{ kJ mol}^{-1} + 297$
$\Delta H°_r = -99 \text{ kJ mol}^{-1}$

Question 69.
For the reaction at 298 K : $2A + B \rightarrow C$
$\Delta H = 400 \text{ J mol}^{-1}$ $\Delta S = 0.2 \text{ JK}^{-1} \text{ mol}^{-1}$
Determine the temperature at which the reaction would be spontaneous.

Answer:
Given,
T = 298K
$\Delta H = 400 \text{ J mol}^{-1}$

$\Delta S = 0.2\ J\ K^{-1}\ mol^{-1}$
$\Delta G = \Delta H - ThS$
if T = 2000K
$\Delta G = 400 - (0.2 \times 2000) = 0$
if T > 2000 K
ΔG will be negative.
The reaction would be spontaneous only beyond 2000 K.

Question 70.
Find out the Value ofequilibrium constant for the following reaction at 298K,
$2\ NH_{3(g)} + CO_{2(g)} \rightleftharpoons NH_2CONH_{2(aq)} + H_2O_{(l)}$
Standard Gibbs energy change, AGr° at the given temperature is – 13.6 kJ mol^{-1}.

Answer:
Given,
T = 298 K
$\Delta G_r^\circ = -13.6\ kJ\ mol^{-1}$
$= -13600\ J\ mol^{-1}$
$\Delta G^\circ = -2.303\ RT \log K_{eq}$

$$\log K_{eq} = \frac{-\Delta G^\circ}{2.303RT}$$

$\log K_{eq} = 2.38$
$K_{eq} = \text{anti} \log(2.38)$
$K_{eq} = 239.88.$

Question 71.
A gas mixture of 3.67 lit of ethylene and methane on complete combustion at 25°C and at I atm pressure produces 6.11 lit of carbon dioxide. Find out the amount of heat evolved in kJ, during this combustion. ($\Delta H_C(CH_4) = -890$ kJ mol^{-1} and ($\Delta H_C(C2H_4) = -1423$ kJ mol^{-1}.

Answer:
Given,
$\Delta H_C\ (CH_4) = -890\ kJ\ mol^{-1}$
$\Delta H_C\ (C_2H_4) = -1423\ kJ\ mol^{-1}$
Let the mixture contain x lit of CH_4 and (3.67 – x) lit of ethylene.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

x lit x lit

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

(3.67−x)lit 2 (3.67 − x) lit

Volume of carbon dioxide formed x + 2 (3.67 – x) 6.11 lit

x + 7.34 – 2x = 6.11

x = 1.23 lit

Given mixture contains 1.23 lit of methane and 2.44 lit of ethylene, hence

$$\Delta H_r^0 = \left[\left(\Delta H_f^0\right)_{products} - \left(\Delta H_f^0\right)_{reactants}\right]$$

$$\Delta H_r^0 = \left[2\left(\Delta H_f^0\right)_{CO_2} + 3\left(\Delta H_f^0\right)_{H_2O}\right] - \left[1\left(\Delta H_f^0\right)_{C_2H_5OH} + 3\left(\Delta H_f^0\right)_{O_2}\right]$$

$$\Delta H_r^0 = \begin{bmatrix} 2\ \text{mol}(-393.5)\ \text{kJ mol}^{-1} \\ +3\ \text{mol}(-285.5)\ \text{kJ mol}^{-1} \end{bmatrix} - \begin{bmatrix} 1\ \text{mol}(-277)\ \text{kJ mol}^{-1} \\ +3\ \text{mol}(0)\ \text{kJ mol}^{-1} \end{bmatrix}$$

$\Delta H_C = [-48.87\ \text{kJ mol}^{-1}] + [-155\ \text{kJ mol}^{-1}]$

$\Delta H_C = -203.87\ \text{kJ mol}^{-1}$